

## POROUS $\gamma$ -ALUMINA MEMBRANES MODIFIED WITH ULTRAFINE ZIRCONIA PARTICLES PREPARED BY REVERSED MICELLES METHOD

Katsuki Kusakabe, Takeyuki Yamaki, Hideaki Maeda and Shigeharu Morooka  
Department of Chemical Science and Technology,  
Kyushu University, Fukuoka 812 Japan

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### INTRODUCTION

Inorganic membranes have great potential as gas separation devices at elevated temperatures, but they have been little used to date. A major reason is that selectivity and permeability of inorganic membranes are not simultaneously achieved at an acceptable cost. If a high selectivity is requested in gas separation process, micropores in the membrane should be close to the size of gas molecules. This often reduces the permeability of that membrane. Porous inorganic membranes obtainable commercially have pore diameters ranging from 4 to 50 nm, where permselectivity is fundamentally controlled by Knudsen diffusion mechanism. Thus it is essential to develop a new membrane that shows an enough selectivity among small molecule gases without sacrificing the permeability.

In the present study, the outer surface of an  $\alpha$ -alumina support membrane is coated with a thin layer of  $\gamma$ -alumina particles prepared by a sol-gel method. Further, micropores of the  $\gamma$ -alumina are narrowed with ultrafine  $\text{ZrO}_2$  particles formed by a reversed micelles technique. The membrane obtained is evaluated with gas separation tests.

### FORMATION OF ULTRAFINE ZIRCONIA PARTICLES

Zirconium tetrabutoxide ( $\text{Zr}(\text{OC}_4\text{H}_9)_4$ , Tri-chemicals) was used as zirconia source. The surfactant was dioleoyl phosphoric acid (DOLPA), which was synthesized according to the method of Goto et al. (1989). Water content in reversed micelles formed with DOLPA was decreased by two orders of magnitude when the pH value was decreased from 6 to 3.5 (Goto et al. 1990). This implies the reversed micelles can be destroyed by acidification.

**Figure 1** shows the flow chart for the production of ultrafine zirconia particles by the reversed micelles technique. Ammonia and KCl was dissolved in a part of water to optimize ionic strength and pH. The same part of isooctane, in which DOLPA was dissolved, was placed on the top of the aqueous solution, and the aqueous phase was gently stirred at 303 K for 24 h. Stable reversed micelles were formed in the isooctane phase, which was recovered with a separation funnel. A butanol solution of zirconium tetrabutoxide was mixed to the isooctane solution. Zirconium tetrabutoxide was transferred to micro water pool in reversed micelles and then hydrolyzed to zirconia. After stirred at 303 K for 24 h, the reversed micelles were destroyed by adding an aqueous nitric acid solution, and finally the organic and aqueous phases were separated.

The concentration of zirconium in the aqueous phase was tried to determine with ICP-AES (SEIKO I. SPS-1200VR), but no zirconium was detected. It was also impossible to recover

zirconia particles into the aqueous solution by adding copper or nickel ions forming strong coordination bond with normal surfactants. The presence of zirconium in the organic phase, on the other hand, was confirmed by x-ray luminescence analysis. These results mean that ultrafine zirconia particles were stabilized in the organic phase with DOLPA molecules coordinated to hydroxyl group of zirconia.

The average size of water pools formed in the organic phase was 5 nm from the results of the dynamic laser scattering measurement (Photol DLS-7000). If one zirconia particle is formed in each micelle, the particle size, calculated from the number of micelles formed, is on the order of 0.1 nm. Since the zirconia concentration in the organic phase is as low as  $3.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ , the size of the particles formed in the reversed micelles is estimated to be less than 1 nm. This was assured from the observation of zirconia particles with a TEM (JOEL JEM-200CX).

#### PREPARATION OF COMPOSITE MEMBRANE

Porous  $\alpha$ -alumina hollow fibers supplied by NOK Corp. were used as the support. The outer surface of the support was coated with a thin layer of  $\gamma$ -alumina by the following procedure: A boehmite ( $\gamma\text{-AlOOH}$ ) sol was formed by adding aluminium isopropoxide into water and peptizing the suspension with hydrochloric acid (Yoldas, 1975). The concentration of the sol was  $0.6 \text{ Al} \cdot \text{mol} \cdot \text{L}^{-1}$ . The hollow fiber, whose lower end was closed, was dipped in the sol for several minutes, dried overnight in the atmosphere and heated to 1023 K at  $50 \text{ K} \cdot \text{h}^{-1}$  in an air stream. This dipping-firing procedure was repeated 4 times.

The concept of modifying the  $\gamma$ -alumina membrane with zirconia particles is illustrated in Fig. 2. The  $\gamma$ -alumina-coated hollow fiber support, one end was plugged and the other was connected to a vacuum line, was dipped in the organic phase where zirconia particles were suspended. Ultrafine zirconia particles were trapped in the  $\gamma$ -alumina layer by suction for 1 h. The treated hollow fiber was heated at  $50 \text{ K} \cdot \text{h}^{-1}$  and kept at 673 or 873 K in an air stream. This procedure was repeated 6 times.

#### GAS PERMEATION

Gas permeation experiments were performed at 373-673 K using hydrogen, nitrogen and methane. The unnecessary surface of the support fiber except for the test part was coated with a  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  sealant. The permeating gas from the outside to the inside of the membrane was carried with argon. The flow rate was measured with a soap-film flow meter, and gas compositions were analyzed by gas chromatography. The total pressure in the both side of the membrane was kept at atmosphere pressure.

The gas permeability largely decreased with increasing number of dipping-firing cycle when the calcination was carried out at 673 K for 2 h. The membrane surface was grayish, and it was suspected that micropores were blocked with carbonaceous matters which were not removed at this temperature. Then the calcination temperature was raised to 873 K. As shown in Fig. 3, the gas permeability remained at about 5 % of that of the initial  $\gamma$ -alumina membrane after six repetitions of the dipping-firing cycle, and was still larger than that of Vycor glass membranes (Tsapatsis et al., 1991). From the observation of a fractured

section with an FE-SEM (Hitachi S-900), the thickness of the  $\text{ZrO}_2/\gamma\text{-Al}_2\text{O}_3$  layer hardly changed after the six repetitions. The line analysis of Zr across the fractured surface indicates that most of  $\text{ZrO}_2$  particles were collected in micropores of the  $\gamma$ -alumina layer. The top surface of the membrane was gradually smoothed by repeating the impregnation cycle.

**Figure 4** shows the effect of the zirconium concentration, based on the volume of the organic phase, on the permeability after three or six repetitions of the dipping-firing cycle. The permeability decreased with increasing zirconium concentration in the range lower than  $2 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ . Smaller particles were packed more tightly in micropores, and the selectivity for hydrogen became large. In the present experiment, the separation factor of hydrogen to nitrogen was about 4.5 after the sixth impregnation cycle at a zirconia concentration of  $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$  as shown in **Fig.5**. The separation factor obtained exceeded the value of the  $\gamma$ -alumina membrane, 3.4. The gas permeability was independent of the pressure drop across the membrane and the permeation temperature.

## CONCLUSION

Ultrafine zirconia particles were formed by hydrolysis of zirconium tetrabutoxide in reversed micelles with a novel surfactant, DOLPA. By repeating the dipping-firing cycle, micropores of a  $\gamma$ -alumina membrane were plugged with the zirconia particles. The permeability of the membrane was ca. 5 % of that of the initial  $\gamma$ -alumina membrane after the six repetition. The permselectivity of hydrogen to nitrogen was increased to 4.5 from the initial value 3.4. The membrane was stable at 673 K.

## REFERENCES

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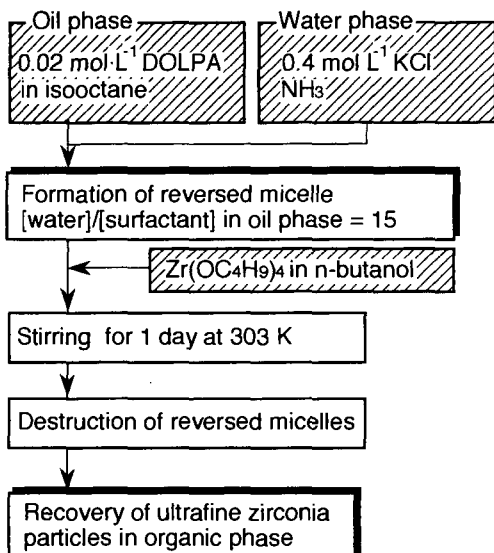


Fig. 1 Preparation of ultrafine zirconia particles by reversed micelles method

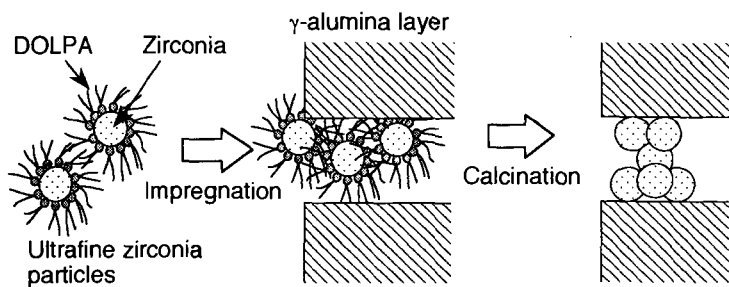


Fig.2 Preparation of zirconia/γ-alumina membrane

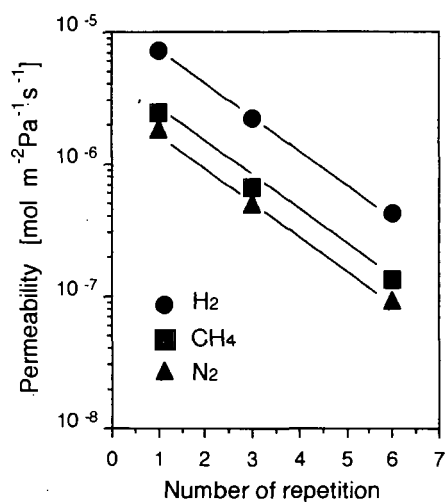


Fig. 3 Effect of repetition number of dipping-firing cycle on gas permeability. Permeation temperature = 373K, Zirconium concentration in organic phase =  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$

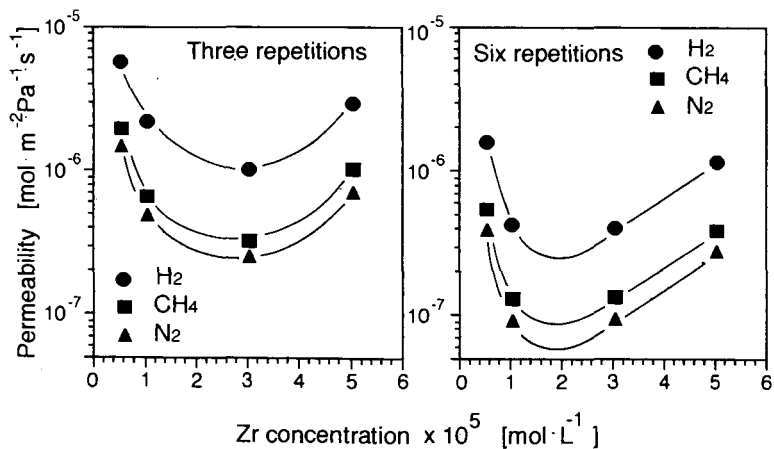


Fig. 4 Effect of zirconia concentration in organic phase on gas permeability. Permeation temperature = 373 K

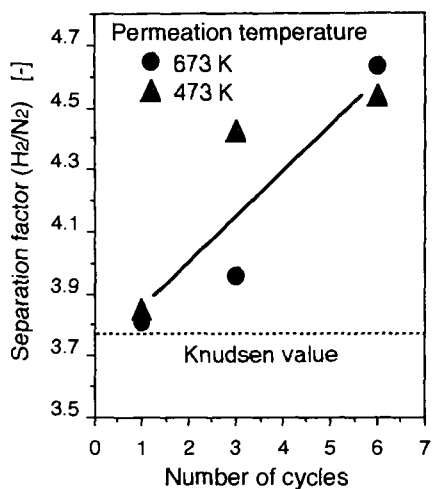


Fig. 5 Effect of repetition number of dipping-firing cycle on separation factor. Zirconium concentration in organic phase =  $1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$